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Fabrication of nanostructured platinum with multilevel porosity for low impedance biomedical recording and stimulation electrodes

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Abstract

We report a new lithography-free technology to fabricate porous metal electrodes *with multiple levels of porosity,* from macroporous – about 1 µm pore diameter – down to nanoporous – 3 nm diameter. The hierarchical combination of mesopores and nanopores allows deeper layers of the electrode to be better accessible for the liquid the electrode is immersed in, aiming to further reduce the impedance of microscale electrodes for biomedical applications. Up to 1000x reduction in impedance was measured in the first experiments, combined with a 230x increase in charge injection capacity. Next to presenting the new and widely applicable (beyond Pt) fabrication process, this is also the first time hierarchical porosity is used in biomedical electrode fabrication.

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Keywords:

1. Introduction

Electric nerve stimulation is a technique more and more used in the biomedical field. Its current applications include alleviating pain, the symptoms of Parkinson's disease and some psychiatric disorders. Electric nerve stimulation is also essential in brain-computer interfacing research, and in a wide range of medical treatments currently under investigation. In many of the new applications under research, not just a small manifold of relatively large electrodes but rather large electrode arrays containing hundreds or thousands of microelectrodes will be used. This opens the way for more accurate, high-resolution neurostimulation but it puts more strain on the design and material selection of the electrodes themselves. In particular, the electrode-tissue interface impedance (i.e. electrode impedance) goes up as the designed electrode area goes down, which has implications both for recording as well as

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for electrical stimulation. Also, as every type of electrode has a charge injection limit per unit of area, the injectable charge per electrode diminishes. To alleviate these problems, several electrode materials have been proposed to replace the classic flat titanium, stainless steel, platinum or gold electrodes that are in common use. These electrodes typically rely on increasing the surface area by porosity, and/or on reversible switching between oxidation states to improve charge injection and impedance.

These technologies include the use of porous platinum (platinum black), porous iridium oxide (deposited as such by e.g. sputtering or electrochemically created in a smooth layer by iodization) [1], TiN, carbon-based electrodes such as CNT fields [2] or conductive polymer based electrodes such as PEDOT [3].

However, the mostly uniform porosity created by the techniques mentioned above still fails to make full use of the third dimension, as increasing the layer thickness above approximately 500 nm does not yield much effect anymore due to limited penetrability [4], as the surrounding liquid cannot reach deeper layers easily.

Therefore, we explore the use of *hierarchical porosity* in biomedical electrodes. A novel versatile fabrication process for hierarchically porous Pt electrodes is presented, together with the first measurement results.

2. Experiments

2.1. Fabrication of electrode with hierarchical porosity

In the first steps, an hierarchally porous silica structure Zeotile-4, a three-dimensional (3D) ordered mesoporous silica material with 2 types of mesopores as well as micropores has been created via a dual template approach [5-9].
The synthesis steps go as follows:

- Colloidal zeolite precursors called nanoslabs are prepared by structuring tetraethylorthosilicate (TEOS) around tetrapropylammonium template (TPA).
- This zeolite precursor solution and surfactant (Pluronic P123 ethylene oxide(EO)-propylene oxide (PO) triblock copolymer) are mixed under acidic conditions
- After 4 days at 90 °C, a solid product forms and is separated by centrifugation.
- The product is washed, dried and baked at 350°C, forming a porous silica structure

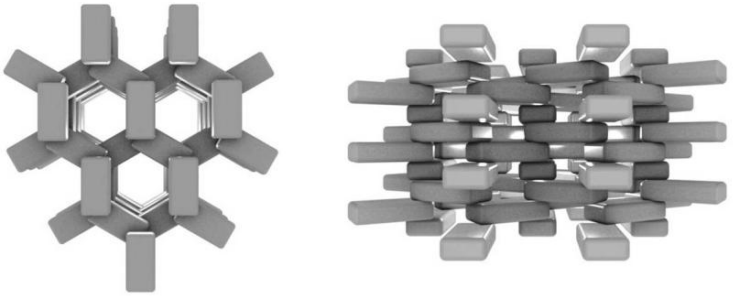

Fig. 1.Hierachical structure representation of Zeotile-4 material. Left; view along the main mesopores right; sideways view on the slit-like small meso pores (reproduced from [9])

In further processing, the porous silica structure is filled with platinum by atomic layer deposition (ALD). Then, the silica backbone is dissolved in diluted hydrogen fluoride. The resulting platinum nanopowder is washed and dried. The multilevel porosity of the resulting power becomes clear during SEM inspection as shown in figure 2: the porosity hierarchy goes from several micrometer-sized pores down to pores a few nanometer in diameter.

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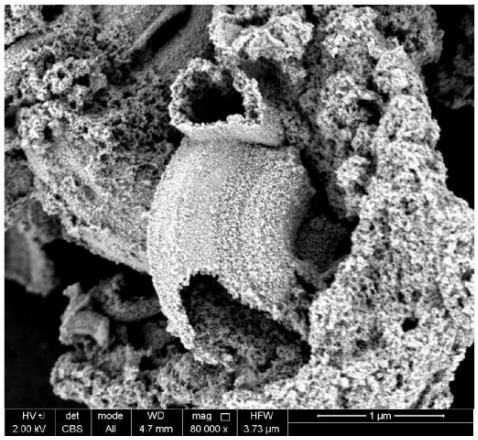

Fig. 2. After ALD deposition of platinum and removal of the silica template by HF treatment, a hierarchically porous conductor remains. SEM pictures reveal the hierarchical porosity of the remaining platinum, with pores down to 3 nm.

This nanopowder was then applied to thin-film platinum test electrodes with $0.019\ cm^2$ surface area that were fabricated by using traditional lithographic microfabrication technology: their fabrication process comprises lift-off processing using a LOR10B and S1818 bilayer resist and sputtering of 150 nm Pt, spin coating of PI-2611 polyimide isolation, opening the isolation above bondpads and electrode contacts by reactive ion etching with oxygen using a thick photoresist mask.

Nanopowder application was done by micropipetting a 3 wt% suspension of the powder on the electrodes heated to 90 °C to accelerate drying, followed by a sintering step of up to 5 hours at 575 °C . SEM inspection after sintering has shown that the hierarchical porosity was maintained.

As an alternative to deposition by micropipetting, the suspension of the powder in a paste suitable for screen printing was investigated. In this paste, polyethylene Carbonate (PEC) dissolved in GBL was used as binder. As PEC decomposes around 250°C, the paste can be used for low-temperature sintering processes. However, as the resulting layers were relatively thin and the nanopower was not uniformly distributed, this technique was left for further research.

2.2. Electrical performance measurements

The fabricated test electrodes were put into phosphate buffered saline water (Invitrogen Gibco, pH 7.2) and electrical measurements were done using a Solartron SI 1255 frequency response analyser and a SI 1287 electrochemical interface. A platinum wire was used as counter electrode and a Ag/AgCl electrode was used as reference. Impedance spectroscopy was done by applying a 0.1V amplitude sine wave, and scanning between 0.1 and 1 MHz. Cyclic voltammetry used to estimate charge injection capacity, and was done by scanning at 100 mV/sec.

Both uncoated and coated test electrodes were tested and the results were plotted in figures 3 and 4. On those figures, it can be seen that the low-frequency impedance of the electrodes is reduced by three orders of magnitude. Furthermore, the charge injection capacity of the coated electrodes was a factor 230 higher. The achieved impedance appears to be superior to regular porous platinum as found in the consulted literature [10-12] by a factor of 5.

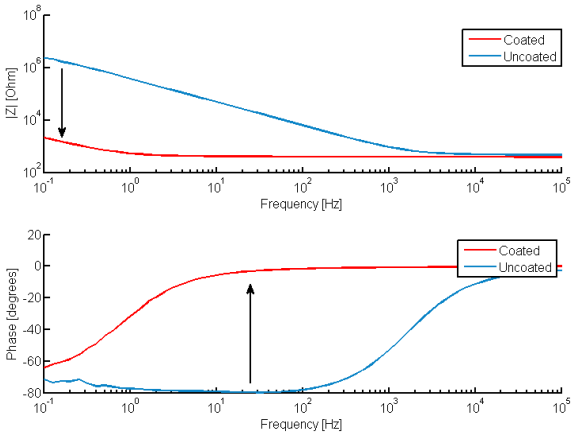

Fig. 3. Measured impedance spectrum showing a factor 1000 improvement at low frequencies.

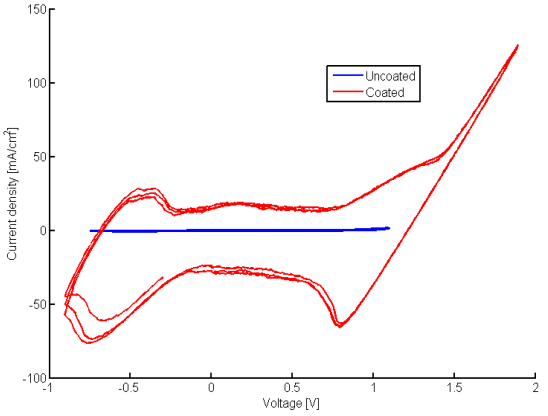

Fig. 4. C*harge storage capacity increases with a factor 230 after coating with the zeotile. Cyclic voltammogram measured at 100 mV/sec.*

3. Discussion and conclusion

We have shown a novel way of fabricating platinum electrodes with high surface area. Adding multilevel porosity improves electrode impedance by up to three orders of magnitude with respect to a plain electrode, and improves the performance with respect to regular, non-hierarchically porous electrodes as well. The resulting electrode material is widely applicable, beyond the field of neurostimulation. In fields such as battery research, supercapacitor research and fuel cells, a similar need for high surface area electrode materials exists. The technique we have shown is not limited to Pt as a variety of metals can be deposited by ALD. This, combined with the fact that no area-limiting lithography is required, makes the electrode fabrication method presented promising for a wide range of applications.

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